

# Oxyanion Adsorption And Competition: A Synchrotron Far Infrared Spectroscopy Study

C. Melendres (Argonne Nat. Lab.), F. Hahn (U. Poitiers, France) and G. Bowmaker (U. Auckland, N.Z.)

Abstract No. mele2047

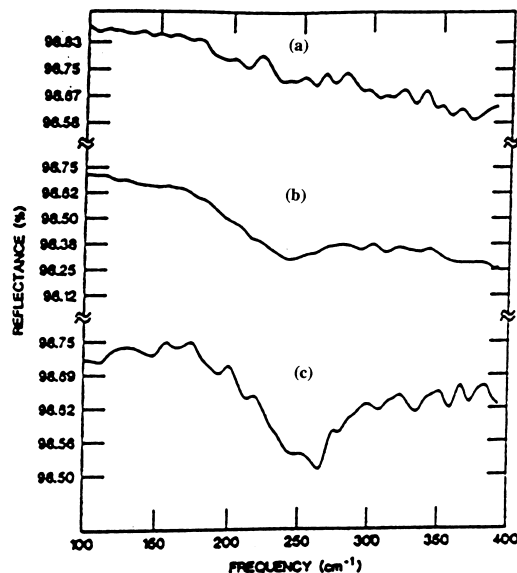
Beamline(s): U4IR

**Summary:** Synchrotron Far Infrared Reflectance Spectroscopy (SFIRS) has been used to study the adsorption of oxyanions at a gold thin-film electrode.

**Results:** Surface-adsorbate vibrational frequencies of 240 and 255  $\text{cm}^{-1}$  have been measured "in-situ" in acid solutions of 0.5 M  $\text{HClO}_4$  containing 0.05 M  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_3\text{PO}_4$  respectively. It was observed that in the presence of  $\text{Br}^-$ , competitive adsorption occurs such that phosphate is displaced from the electrode surface and the current-potential behavior of the electrode is determined by the more strongly adsorbed  $\text{Br}^-$  anion. In 0.1 M  $\text{NaClO}_4$  at neutral pH, no interaction between the oxyanions and the gold surface could be observed and the intensity of the  $\text{Au-Cl}^-$  vibration was about five times weaker than in acid. Adsorption of  $\text{OH}^-$  was found to be the dominant interaction, inhibiting sulfate adsorption, in 0.05 M  $\text{Na}_2\text{SO}_4$  + 0.1 M  $\text{NaClO}_4$  solution. The latter finding is similar to results obtained by others on the inhibition of sulfate adsorption on silver by  $\text{OH}^-$ .

**Conclusions:** SFIRS is a powerful technique for the study of the behavior of adsorbed species at the electrode/electrolyte interface.

**Acknowledgments:** We thank the Office of Science and Office of Environmental Research of the U.S. Department of Energy (Contract No. W-31-109-ENG-38), CNRS-UMR 6503 (Electrocatalysis Group, Univ. Poitiers), NATO Science and Environmental Affairs Division (Grant No. 920512), and the University of Auckland Research Committee for financial assistance, and G.P. Williams (NSLS) for assistance with the U4IR beamline and for many helpful discussions.



**Figure 1.** "In-situ" synchrotron far IR reflectance spectra of a gold thin film electrode in 0.5 M  $\text{HClO}_4$  + (a) 0.05 M  $\text{KNO}_3$ , (b) 0.05 M  $\text{Na}_2\text{SO}_4$ , and (c) 0.05 M  $\text{Na}_3\text{PO}_4$